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(12) Patent: (11) CA 911135

(54) CATALYST FOR LOW TEMPERATURE WATER GAS SHIFT REACTION

(54)

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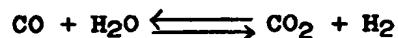
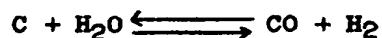
ABSTRACT:

ABSTRACT OF THE DISCLOSURE

Low temperature water gas shift reaction using catalyst comprising at least one alkali metal salt of an acid having an ionization constant below  $1 \times 10^{-3}$  and at least one metal or compound of a metal from Groups VB, VIB, or VIII of Periodic Table.

1        This invention relates generally to a process for  
2 producing hydrogen by reacting carbon monoxide with steam at  
3 elevated temperatures in the presence of at least one alkali  
4 metal compound and at least one element of Groups VB, VIB or  
5 VIII of the Periodic Table of Elements. More particularly,  
6 the invention relates to a process for producing hydrogen by  
7 reacting carbon monoxide with steam at a temperature of at  
8 least 300°F. in the presence of an alkali metal compound de-  
9 rived from an acid having an ionization constant less than  
10  $1 \times 10^{-3}$  with at least one element of Groups VB, VIB or VIII  
11 of the Periodic Table of Elements.

12      The present invention relates to the preparation of  
13 hydrogen from carbonaceous materials in accordance with the  
14 equations



17      It is well known to prepare hydrogen by reacting  
18 carbonaceous materials, such as hydrocarbons with steam at  
19 elevated temperatures of 1200°-1400°F. or coal or coke with  
20 steam at temperatures up to 2500°F. and then to react the re-  
21 sulting mixture of CO and H<sub>2</sub> with more steam at lower tempera-  
22 tures, for example at 800°-900°F. in the presence of suitable  
23 catalysts to convert the carbon monoxide produced in the first  
24 stage to carbon dioxide and additional hydrogen. The second  
25 step, known as the water gas shift reaction, is limited by  
26 equilibrium considerations and complete conversion of CO to  
27 CO<sub>2</sub> is not realized. However, the concentration of CO in the  
28 product when equilibrium is reached is highly dependent on the  
29 temperature. Consequently conversions can be increased by  
30 either removing the carbon dioxide and again contacting the CO  
31 and steam with the catalyst in the same or subsequent stages  
32 or by lowering the temperature.



1           The effect of temperature on the equilibrium con-  
 2 stant  $K = (CO_2)(H_2)$  is shown in the following table.  
 3           (CO) (H<sub>2</sub>O)

7	°F.	K	Concentration of CO at Equilibrium (dry basis) Feed*	
			A	B
8	900	5.61		
9	800	9.03	5.19	
10	700	15.89	3.30	1.12
11	600	31.44	1.77	0.56
12	500	72.75		
13	400	206.8	0.29	

14 \* A - 50% of a 1/1 H<sub>2</sub>/CO mixture + 50% H<sub>2</sub>O (steam)  
 15       B - 30% of a 1/1 H<sub>2</sub>/CO mixture + 70% H<sub>2</sub>O (steam)

16           It is thus evident that less CO will remain uncon-  
 17 verted and costly methods of operation will be avoided by  
 18 operating at as low temperatures as possible, e.g., 300°-700°F.,  
 19 preferably 400-600°F. Such low temperatures can be employed  
 20 by the use of a catalyst consisting of copper deposited on  
 21 zinc oxide. Unfortunately, however, this catalyst will not  
 22 tolerate even traces of sulfur in the feed. Since coal and  
 23 coke and heavy hydrocarbon feeds suitable for conversion to  
 24 hydrogen contain appreciable amounts of sulfur, e.g., up to  
 25 5 to 10 wt. %, which is converted to hydrogen sulfide and even  
 26 some small amounts of carbon disulfide and carbonyl sulfide,  
 27 these feeds are precluded from use with the Cu-ZnO catalyst,  
 28 and are limited to shift temperatures of 750°-900°F. using a  
 29 sulfur resistant catalyst such as Fe<sub>2</sub>O<sub>3</sub> promoted with Cr<sub>2</sub>O<sub>3</sub>.  
 30 It is also known to use K<sub>2</sub>CO<sub>3</sub> deposited on activated carbon  
 31 as a low temperature catalyst (see Erdol u. Kohle V. 6:195  
 32 (1953) and V. 9:19 (1956)).

It has now been found that gas mixtures containing carbon monoxide contaminated with relatively large amounts of sulfur can be converted to hydrogen economically by reaction with steam at a temperature of at least 300° F. in the presence of (1) at least one alkali metal compound, said compound being derived from an acid having an ionization constant less than about  $1 \times 10^{-3}$ , and (2) a hydrogenation-dehydrogenation component selected from the group consisting of metal compositions comprising vanadium, molybdenum, tungsten or cobalt materials, and mixtures of metal compositions comprising a vanadium, molybdenum, tungsten or cobalt material admixed with a nickel, iron or chromium material. The alkali metal compound and the hydrogenation-dehydrogenation component may be supported on a carrier together or separately. In addition, the alkali metal compound may be impregnated on the hydrogenation-dehydrogenation component. Particularly suitable hydrogenation-dehydrogenation components are one or more of said elements of Groups VB, VIB or VIII of the Periodic Table of Elements used either alone or in combination, such as said Group VIII metals in combination with said metals of Group VB with or without said metals of Group VIB. These catalysts have especially good activity if they are sulfided prior to use, and thus are particularly suitable for use with feeds containing sulfur. However, these catalyst compositions may also be used with sulfur-free feeds. When sulfur-containing feeds are used the catalyst may be sulfided in situ by passing the feed over the oxide or other compound which is then converted to the sulfide. The ratio of said groups VB, VIB or VIII metal component to the alkali metal compound is from about 0.001 to about 10 parts by weight of the alkali metal compound.

The first stage reaction in the preparation of hydrogen consists in reacting coal, coke, or heavy feeds at 1000-2500° F. with steam with or without the presence of hydrogen or the reaction of natural gas or other hydrocarbons with

1 steam in the presence of reformer catalysts containing nickel,  
2 cobalt, etc. promoted with magnesia, alumina, thoria and  
3 similar oxides and supported if desired on an inert base at  
4 temperatures of 1200-1600°F. Hydrogen, carbon dioxide and  
5 carbon monoxide are obtained with a high ratio of CO to CO<sub>2</sub>.

6 The present invention makes it possible not only to  
7 overcome the effect of sulfur on the alkali metal compounds  
8 but also enables substantially complete conversion of carbon  
9 monoxide to carbon dioxide to be achieved in one step at low  
10 temperatures, an accomplishment which has heretofore been  
11 impossible in the presence of sulfur. These results are ob-  
12 tained in accordance with the present invention by carrying  
13 out the reaction in the additional presence of 0.001 to 10  
14 parts by weight of a hydrogenation-dehydrogenation catalyst  
15 component per weight of alkali metal without reference to any  
16 support which may be used. The use of these catalysts in  
17 conjunction with the alkali metal salt enables more complete  
18 conversion of the carbon monoxide to carbon dioxide even in  
19 the presence of sulfur and thus affords vast economic savings  
20 since a costly step of removing the carbon dioxide is avoided.  
21 While it is not intended to be limited by any theory concern-  
22 ing the mechanism of the reaction, it is believed that the  
23 alkali metal component in the presence of water vapor exists  
24 as a liquid phase in contact with the surface of the hydro-  
25 genation-dehydrogenation component. It is believed that the  
26 aqueous alkali metal phase converts the carbon monoxide to  
27 formate and the hydrogenation-dehydrogenation catalyst surface  
28 converts the formate into CO<sub>2</sub> and H<sub>2</sub>. Thus the interaction  
29 between the two types of catalysts brings about a vast syner-  
30 gistic effect on catalytic activity.

31 Suitable alkali metal components include the carbon-  
32 ate, bicarbonate, biphosphate, sulfide, hydrosulfide, silicate,

1 bisulfite, aluminate, hydroxide, acetate, tungstate, etc. of  
2 sodium, potassium, lithium, rhubidium and cesium. In addition  
3 the alkali metal salts of organic acids such as acetate are  
4 equally suitable. Actually the alkali salt of any acid which  
5 has an ionization constant of less than  $1 \times 10^{-3}$  may be used.  
6 The potassium and cesium salts are most preferred.

7 The hydrogenation-dehydrogenation component of the  
8 catalyst comprises one or more of the elements of Groups VB,  
9 VIB and VIII of the Periodic Table (designed by Henry D.  
10 Hubbard and revised 1956 by William F. Meggers of the National  
11 Bureau of Standards). Vanadium, chromium, molybdenum, tung-  
12 sten, iron, nickel, or cobalt may be used alone, but mixtures  
13 of iron, nickel or cobalt with the vanadium, chromium, molyb-  
14 denum or tungsten are particularly suitable.

15 If the metals of Groups VB, VIB and VIII are used  
16 with sulfur-containing feeds, they may be used in the form of  
17 the oxide or other compound easily sulfided. These compounds  
18 are then sulfided in situ by passing the sulfur-containing  
19 feed over them. Cesium or potassium carbonate or acetate com-  
20 bined with cobalt-molybdenum is a particularly effective cata-  
21 lyst. The iron, cobalt and nickel sulfide (Group VIII metal)  
22 or the vanadium sulfide (Group VB) or the chromium molybdenum  
23 and tungsten sulfide (Group VIB) may be used individually  
24 together with the alkali metal if desired. Hereinafter these  
25 catalysts will be referred to as the metal without reference  
26 to how it is combined since the actual composition prior to  
27 the shift reaction is, for example, cobalt oxide-molybdenum  
28 oxide-aluminum oxide and the like. Under the reaction condi-  
29 tions the catalyst usually exists in a partially reduced and  
30 sulfided state which is difficult to define stoichiometrically  
31 and thus a description using the active metallic elements is  
32 as accurate as any.

1       The catalytically active metal components may be  
2   used either supported or unsupported and in the former case  
3   the nature of the carrier is not critical. Suitable carriers  
4   include alumina having an extremely broad range of surface  
5   areas, such as gamma and alpha aluminas. Other suitable sup-  
6   port materials include silica, silica-alumina, e.g., silica-  
7   alumina cogel cracking catalysts; zeolites such as faujasite,  
8   erionite, and the like; activated carbon, coconut charcoal,  
9   Columbia L carbon, magnesia, titania, zirconia and the like.  
10   Particularly suitable gamma and alpha-alumina catalyst sup-  
11   ports are available commercially. Such supports may be pre-  
12   pared by a variety of methods. For example they may be pre-  
13   pared by hydrolyzing an aluminum alcoholate which may have  
14   been prepared in accordance with the disclosures of U.S.  
15   Patent 2,636,865. They may also be prepared by precipitating  
16   a hydrous alumina from an aqueous solution of an aluminum salt,  
17   preferably  $\text{AlCl}_3$ . A third method of preparation comprises  
18   dissolving metallic aluminum in weakly acidified water, pref-  
19   erably acidified with an organic acid, such as acetic acid,  
20   in the presence of mercury or compound thereof, and thereafter  
21   gelling the alumina sol thus formed. The hydrous alumina  
22   prepared by any of the foregoing procedures is subsequently  
23   dried and calcined at temperatures between 600 and 1200°F.,  
24   preferably between 900 and 1000°F.

25       The catalyst components can be incorporated on the  
26   support in any conventional manner. Preferably the hydro-  
27   genation-dehydrogenation components are placed on the support  
28   first and this combination is then calcined, e.g., at 1000-  
29   1200°F., to convert the metals to the stable oxide forms.  
30   Then the alkali metal, e.g., cesium or potassium carbonate,  
31   is impregnated onto the support and the catalyst simply dried.  
32   In general the carrier material is impregnated with a solution

1 containing the desired compound. The finished catalyst is  
2 then sulfided in a known manner, e.g., by passing over the  
3 catalyst a mixture of hydrogen and hydrogen sulfide, carbon  
4 disulfide, butyl mercaptan and the like. However, it may be  
5 sulfided in situ as described above.

6 Alternatively the various components may be mixed  
7 by mechanical means, such as by dry mixing. Good catalysts  
8 can be obtained by fine milling of a cobalt-molybdenum catalyst  
9 supported on alumina and mixing the powder obtained with a  
10 powdered alkali metal compound such as cesium carbonate. The  
11 resultant mixture, after the addition of a lubricant such as  
12 stearic acid or graphite, is compressed into pellets which can  
13 be calcined and sulfided.

14 The hydrogenation-dehydrogenation component is used  
15 in amounts varying from about 0.001 to about 10 parts by  
16 weight based on the alkali metal compound, preferably from  
17 about 0.01 to about 5.0 parts by weight and most preferably  
18 from 0.1 to 3.0 parts by weight, exclusive of any carrier  
19 which might be used to support either or both components. All  
20 components are calculated on the basis of the oxide thereof.

21 When a carrier is used the ratio of catalyst compo-  
22 nents to carrier is not critical but may range from about 90  
23 wt. % to about 0.5 wt. %, however, it has been found most  
24 desirable to use amounts of from about 50 to about 1 wt. %,  
25 all based on total catalyst including the carrier. Hydro-  
26 genation-dehydrogenation catalysts which have been found par-  
27 ticularly effective contain cobalt oxide and molybdenum oxide  
28 on gamma alumina prior to sulfiding. Particularly suitable  
29 ranges of catalyst components are from about 0.1 to about 10  
30 wt. % cobalt oxide and from about 1 to about 25 wt. % molyb-  
31 denum oxide. Most suitable are hydrogenation-dehydrogenation  
32 components present in an amount of from 1 to about 5 wt. %

1 cobalt oxide and from 5 to about 15 wt. % molybdenum oxide.  
2 This catalyst component can then be impregnated with about 5  
3 to about 80 wt. % of alkali metal compound and sulfided to  
4 make the final catalyst. Alternatively, the alkali metal  
5 compound may be itself supported independently of the hydro-  
6 genation-dehydrogenation component, both of which may be  
7 mixed together and then sulfided to make the catalyst composi-  
8 tion.

9 The process is preferably carried out continuously.  
10 The gaseous hourly space velocity can vary within wide limits.  
11 Gaseous hourly space velocities between 300 and 30,000 volumes  
12 of feed per volume of supported catalyst per hour (V/V/Hr)  
13 measured on the basis of dry gas under standard conditions are  
14 particularly suitable for most applications. The process may  
15 be carried out at higher gaseous hourly space velocities if  
16 desired.

17 Referring now more specifically to the shift process,  
18 except for the low temperature, with its favorable effect on  
19 reaction equilibrium, resulting from the practice of this in-  
20 vention, water gas shift reactions are well known. Carbon  
21 monoxide or a gas containing 0.1% or more carbon monoxide by  
22 volume, and steam in an amount of 1-100 volumes per volume of  
23 carbon monoxide, are introduced into a shift converter and  
24 passed over the alkali metal and hydrogenation-dehydrogenation  
25 catalyst at a temperature between 300 and 700°F. The pressure  
26 is preferably in the range of 200 to 1500 pounds per square  
27 inch gauge (psig), although it may vary from atmospheric to  
28 3,000 psig or more. However the exact pressure and tempera-  
29 ture conditions must be maintained above the dew point of the  
30 steam in the mixture. The process is particularly effective  
31 when the feed contains sulfur. In fact the presence of sulfur  
32 in the feed actually results in increased conversions in many

1 cases. If necessary the catalyst may be regenerated by oxida-  
2 tion and resulfiding.

3           Typical results of operations in accordance with  
4 the process of this invention are given in the following exam-  
5 ples. It will be evident that the examples are merely illus-  
6 trative of the invention and no undue limitation is imposed  
7 thereby. In all cases herein the analyses of the hydrogена-  
8 tion-dehydrogenation component are calculated on the basis  
9 of the metals expressed as the oxides and the alkali metal  
10 component expressed as the oxide.

11 EXAMPLE 1

12           A gas mixture consisting of approximately 46% hydro-  
13 gen, 53% carbon monoxide and about 1% H<sub>2</sub>S was used as feed.  
14 This gas feed was passed through a reactor containing a cata-  
15 lyst at 550 psig at such a rate as to maintain an exit dry  
16 gas product rate of 2700 V/V/Hr. measured at room tempera-  
17 ture and 1 atmosphere of pressure and together with the feed  
18 gas was fed steam in the mole ratio of one mole per mole of  
19 dry product gas. The catalyst consisted of cobalt-molybdenum  
20 dispersed on gamma alumina having a surface area of 200-400  
21 M<sup>2</sup>/g. and a pore volume of 0.60-0.70 cc per gram, the cobalt  
22 content corresponding to 3.5 wt. % of CoO and the molybdenum  
23 content corresponding to 13 wt. % MoO<sub>3</sub> and which was impreg-  
24 nated with 44-48 wt. % of cesium acetate in an aqueous solu-  
25 tion ( $1.7 \times 10^{-3}$  moles per cc catalyst volume) and dried at  
26 about 150°C. The catalyst was then sulfided in situ by pass-  
27 ing the feed over the catalyst for about an hour at a tempera-  
28 ture of 625°F. The following results were obtained.

29           TABLE I

30	Run No.	1	2	3
31	Metals	CoMo	CoMo	None
32	Alkali metal compound	Cs Acetate	Cs Acetate	Cs Ace-
33				tate

1                   TABLE I (Continued)

2 Run No.	3 $\gamma$ -alumina support	1 Type A	2 Type B	3 Type B
<u>% CO in Product</u>				
5 Temp.	6 Pressure			
6 °F.	7 psig			
7 625	8 550	9 1.16	10 1.17	11 48.61
8 525	9 550	10 0.53	11 0.54	
9 475	10 550	11 0.43		
10 425	11 550	12 0.32	13 0.40	
11 425	12 200	13 0.31		0.23
12 350	13 200	14 20.57		
13 350	15 0	16 45.54	17 41.35	

14                 The above data show that a mixture of cesium ace-  
 15 tate and cobalt-molybdenum is an extremely effective and effi-  
 16 cient catalyst for catalyzing the water gas shift reaction  
 17 down to temperatures as low as 350°F. This compares very  
 18 favorably with the results obtained with cesium acetate alone  
 19 under the same conditions where 48.61% of carbon monoxide re-  
 20 mained in the product at 625°F. Feed gas and product gas  
 21 analyses are expressed as mol. %.

22               EXAMPLE 2

23                 The experiment of Example 1 was repeated except that  
 24 the cobalt and molybdenum were used separately. The results  
 25 are shown in Table II.

26               TABLE II

27	28 Run No.	29 Metals	30 Pressure	31
		Alkali	psig	Temp.
32	33 625	34 525	35 550	36 4.10
				37 32.83
				38 1.53
				11.56

35                 These two examples illustrate the enhanced effec-  
 36 tiveness of the cobalt-molybdenum combination in contrast to  
 37 each component alone, even though all of these systems are  
 38 effective catalysts in the invention.

1 EXAMPLE 3

2 The experiment of Example 1 was repeated showing the  
 3 effect of varying the alkali metal component when using co-  
 4 balt-molybdenum. The results are reported in Table III.

5 TABLE III

6 Run No.	6	7
7 Metals	CoMo	CoMo
8 Alkali	K Acetate	Cs <sub>2</sub> CO <sub>3</sub>

( $1.7 \times 10^{-3}$   
moles/cc catalyst) ( $8.7 \times 10^{-4}$   
moles/cc catalyst)

11 % CO in Product

12 Temp. °F.	13 Pressure psig	14	15	16	17	18	19	20
625	550	1.19			0.39	0.77	200	0
525	550							
475	550							
425	550							
425	200							
350	200							
350	0							
								43.67

21 The above data show that potassium acetate is sub-  
 22 stantially as effective as cesium acetate down to tempera-  
 23 tures as low as 425°F. and that cesium carbonate is just as  
 24 effective.

25 EXAMPLE 4

26 The experiment of Example 1 was again repeated to  
 27 show the effect of varying the Group VIII metal. The results  
 28 are shown in Table IV.

29 TABLE IV

30 Run No.	9	10
31 Metals	FeMo	NiMo
32 Alkali	Cs Acetate	Cs Acetate

33 % CO in Product

34 Temp. °F.	35 Pressure psig	36	37	38	39
625	550	1.15			1.26
525	550		11.32		0.87
475	550				
425	550				35.07

1       The above data show that nickel-molybdenum and iron-  
 2 molybdenum are also effective catalyst in the carbon monoxide  
 3 reaction.

4       EXAMPLE 5

5       The experiment of Example 1 was again repeated to  
 6 show the effect of varying the Group VB and VIB metals. The  
 7 data are reported in Table V.

8       TABLE V

9	Run No.	12	13	14
10	Metals	CoV	CoCr	CoW
11	Alkali	Cs Acetate	Cs Acetate	Cs Acetate

12       % CO in Product

13	Temp. °F.	Pressure psig		
15	625	550	7.18	17.24
16	525	550	46.08	22.93
				42.41

17       The above data show the effectiveness of vanadium,  
 18 chromium, and tungsten as catalysts when used with cobalt.

19       EXAMPLE 6

20       Run 1 of Example 1 was repeated to determine the  
 21 effect of sulfiding on the effectiveness of the catalyst on  
 22 feeds containing sulfur as well as on sulfur-free feeds. The  
 23 following results were obtained at 625°F.

24       TABLE VI

25	Run No.	16	17	18
26	Catalyst	Unsulfided	Sulfided in situ	Presulfided
27				

28	Feed			
29	H <sub>2</sub>	45.9	46.44	45.9
30	CO	54.1	52.51	54.1
31	H <sub>2</sub> S	0	1.4	0
32	Product			
33	CO	17.32	1.19	1.18
34	CO Conversion %	57.9	96.5	96.7

35       The above data show that the sulfided catalyst  
 36 whether sulfided in situ (Run No. 17) or presulfided with no  
 37 sulfur in the feed (Run No. 18) gives equilibrium conversions

1 of carbon monoxide while the unsulfided catalyst with no sul-  
 2 fur in the feed (Run No. 16) gives much poorer conversion.

3 EXAMPLE 7

4 The conditions of Example 1 were repeated with  
 5 various catalysts to show the effect of varying the type of  
 6 support, using a low surface area alpha Al<sub>2</sub>O<sub>3</sub>, faujasite, and  
 7 carbon as compared to the high surface area gamma alumina of  
 8 Run 2 (Example 1).

9

TABLE VII

10	Run No.	2	19	20	21
11	Support	γ-Al <sub>2</sub> O <sub>3</sub>	Faujasite	α-Al <sub>2</sub> O <sub>3</sub>	Activated Carbon
12					
13	Metals	CoMo (3.5% CoO 13% MoO <sub>3</sub> )	CoMo (3.7% CoO 13.8% MoO <sub>3</sub> )	CoMo (1.6% CoO 6.0% MoO <sub>3</sub> )	Mo (12% MoO <sub>3</sub> )
14					
15	Alkali	Cs Acetate	Cs Acetate	Cs Acetate	Cs Acetate
16					
17	Temp. °F.	Pressure Psig		% CO in Product	
18					
19	625	550	1.17	1.15	1.18
20	525	550	0.54	0.62	0.51
21	475	550			(<1.03)
22	425	550	0.40		
23	425	200	0.23	32.3	
24	350	200			
25	350	0	41.35		

26 EXAMPLE 8

27 When a catalyst containing sodium carbonate and a  
 28 cobalt-molybdenum on alumina hydrogenation-dehydrogenation  
 29 catalyst is used according to Example 1 at 600°F. the CO is  
 30 substantially completely converted to the thermodynamic equi-  
 31 librium concentration of CO<sub>2</sub>.

32 EXAMPLE 9

33 A gas mixture consisting of approximately 46% hydro-  
 34 gen, 53% carbon monoxide and about 1% H<sub>2</sub>S was used as a feed  
 35 gas. This gas feed was passed through a catalyst containing  
 36 reactor at 550 psig at such a rate as to maintain an exit dry  
 37 gas product rate of 2700 V/V/Hr. under conditions of room  
 38 temperature and 1 atmosphere of pressure, and together with

1 the feed gas was fed steam in the mole ratio of 1 mole per  
 2 mole of dry product gas. The cobalt-molybdenum used in this  
 3 experiment was prepared in the same manner and had the same  
 4 percentage composition as that used in Example 1. This co-  
 5 balt-molybdenum component was impregnated with an aqueous  
 6 solution of potassium carbonate ( $K_2CO_3$ ) in an amount equiva-  
 7 lent to  $8.7 \times 10^{-4}$  moles per cc catalyst volume, and was  
 8 dried at about  $150^{\circ}C$ . Based on total catalyst composition  
 9 there was 13.6 weight percent potassium carbonate. The cata-  
 10 lyst was then sulfided by means of a standard method. The  
 11 following results were obtained.

12 TABLE VIII

13	14 Reaction Temp. °F.	15 Reaction Press. psig	% CO in Product	
			Found	Thermodynamic Equilibrium
16	550	550	0.64	0.63
17	425	200	0.20	0.22

18 The above data show the clear advantage of employ-  
 19 ing the potassium carbonate on the hydrogenation-dehydrogena-  
 20 tion component.

21 EXAMPLE 10

22 When Example 9 is repeated, substituting for the  
 23 cobalt-molybdenum a hydrogenation-dehydrogenation component  
 24 comprising 2.30 weight percent CoO, 0.45 weight percent NiO  
 25 and 15.0 weight percent  $MoO_3$  on alumina, a substantially sim-  
 26 ilar, beneficial result is obtained.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A process for the conversion of a gas mixture containing carbon monoxide and steam to hydrogen and carbon dioxide which comprises contacting said gas mixture at a temperature of at least 300°F. with a catalyst comprising (1) an alkali metal compound derived from an acid having an ionization constant less than  $1 \times 10^{-3}$  and (2) a hydrogenation-dehydrogenation component selected from the group consisting of metal compositions comprising vanadium, molybdenum, tungsten or cobalt materials and mixtures of metal compositions comprising a vanadium, molybdenum, tungsten or cobalt material admixed with a nickel, iron or chromium material, at least a portion of said metal material of said catalyst being in sulfided form, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound calculated on the basis of the oxide thereof, being in the range of 0.001:1 to 10:1.
2. The process of claim 1, wherein said alkali metal compound is an alkali metal carbonate.
3. The process of claim 1, wherein said hydrogenation-dehydrogenation component is a sulfided mixture of cobalt and molybdenum materials.
4. The process of claim 3, wherein said alkali metal compound is an alkali metal carbonate.
5. The process of claim 1, wherein said catalyst is supported on a suitable carrier.
6. The process of claim 3, wherein said gas mixture additionally contains a sulfur material.
7. A process for the conversion of a gas mixture contain-

ing carbon monoxide and steam to hydrogen and carbon dioxide which comprises contacting said gas mixture at a temperature from 300-700°F. and at an elevated pressure with a catalyst comprising (1) an alkali metal compound derived from an acid having an ionization constant less than  $1 \times 10^{-3}$  and (2) a hydrogenation-dehydrogenation component comprising (i) sulfided vanadium, molybdenum, tungsten, cobalt or mixtures thereof, or (ii) sulfided mixtures of vanadium, molybdenum, tungsten, cobalt or mixtures thereof with nickel, iron or chromium, said catalyst being supported on a carrier and the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of 0.001:1 to 10:1.

8. The process of claim 7, wherein said alkali metal compound is an alkali metal carbonate.

9. The process of claim 7, wherein said process is conducted at a pressure from 200-3000 psig. and at a space velocity of at least 300 volumes of gas mixture per volume of supported catalyst per hour.

10. The process of claim 7, wherein said alkali metal compound is potassium carbonate.

11. The process of claim 10, wherein said hydrogenation-dehydrogenation component is a sulfided mixture of cobalt and molybdenum materials.

12. The process of claim 7, wherein said gas mixture additionally contains a sulfur material.

13. The process of claim 5, wherein said carrier is alumina.

14. The process of claim 7, wherein said carrier is alumina.

15. A catalyst composition comprising in combination (1) an alkali metal compound derived from an acid having an ionization constant less than  $1 \times 10^{-3}$  and (2) a hydrogenation-dehydrogenation component comprising metal constituents selected from the group consisting of (i) vanadium, molybdenum or tungsten materials alone; (ii) a vanadium material in admixture with a molybdenum, tungsten or cobalt material; (iii) a molybdenum material in admixture with a chromium or tungsten material, (iv) a cobalt material in admixture with a nickel or iron material; **E** and (v) mixtures of tungsten ~~or~~<sup>and</sup> chromium materials, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of 0.001:1 to 10:1.

16. The catalyst composition of claim 15, wherein said catalyst is supported on a suitable carrier.

17. The catalyst composition of claim 15, wherein said alkali metal compound is an alkali metal carbonate.

18. The catalyst composition of claim 17, wherein said alkali metal carbonate is potassium carbonate.

19. The catalyst composition of claim 15, wherein at least a portion of said non-noble metal hydrogenation-dehydrogenation component exists in a sulfided form.



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**SUBSTITUTE**

***REPLACEMENT***

**SECTION is not Present**

***Cette Section est Absente***